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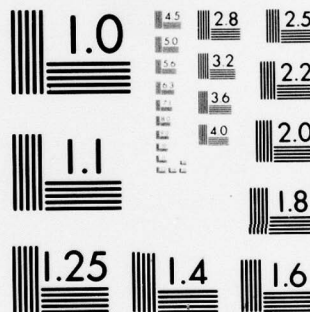UNCLASSIFIED   AFOSR-TR-79-0954   NL

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GROWTH AND CHARACTERIZATION OF EPITAXIAL PIEZOELECTRIC AND SEMICONDUCTOR FILMS

K. M. Lakin, Principal Investigator

and S. K. Tiku

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ABSTRACT

This report includes the details of research work on this two-year project on the growth and characterization of thin films for piezoelectric applications. The report covers the results on AlN and ZnO growth by the metal-organic process. The problems associated with the AlN on sapphire system have been discussed. In the case of ZnO films, low temperature CVD systems (DEZ/H_2O and DEZ/CO_2) have been developed. It is seen that the films grown by the DEZ/CO_2 system do not need any post-growth diffusion, as the as-grown resistivity is quite high.

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I. INTRODUCTION

A. General

Information density carried by a transmission medium is related to the signal wavelength. The shorter the wavelength, the greater the density. Acoustic and laser wavelengths are several orders of magnitude shorter than the shortest electromagnetic microwaves. Because of this there is a great interest in the investigation of acoustic signal processing devices. Compact acoustic delay lines give large signal delays. Surface acoustic waves have the added advantage that the acoustic energy is confined to the surface and the waves can be tapped or otherwise modified while propagating.

Layered media in which a piezoelectric thin film is hetero-epitaxially deposited on a nonpiezoelectric substrate such as sapphire have unique properties and applications. AlN and ZnO films grown on sapphire are of particular interest in this regard.

The major reason for interest in AlN/Al_2O_3 is that this material combination has some very desirable acoustic properties such as high propagation velocity, high coupling coefficient, and low temperature coefficient of delay. The propagation velocity (6 KM/sec for thin AlN films) is nearly twice that of quartz or $LiNbO_3$ and suggest that the fabrication resolution requirement of high frequency devices can be eased. The maximum coupling coefficient of 0.8%, for propagation along the AlN c-axis, is between that of quartz and $LiNbO_3$. Temperature coefficients of delay as low as 24 ppm have been measured at an AlN film thickness to wavelength ratio of 0.6. This together with other measurements suggest that thicker films could produce zero temperature coefficient of delay for

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the composite material.

Other important factors are associated more with the substrate. First, R-plane sapphire is a good substrate for the growth of epitaxial films which are also capable of co-existing with an AlN film. Second, R-plane sapphire is an increasingly less expensive and available substrate due to its use in the production of silicon-on-sapphire integrated circuits. Third, the large area substrates promise AlN films covering areas in excess of 10 square inches; a number unlikely to ever be achieved by bulk AlN wafers because the largest bulk AlN samples measure in the 1-3 mm range.

At first glance then, AlN/Al_2O_3 appears to be a very desirable material of immediate usefulness. However, this material is not without its problems. Specifically, the problem areas for AlN/Al_2O_3 are film thickness uniformity, strain induced warping of the substrate which causes device fabrication errors, coupling coefficient and propagation velocity variations due to imperfections in the film microstructure. These problems are more pronounced as the film thickness increases.

Thin films of ZnO on non-piezoelectric substrates are replacing quartz and lithium niobate in many practical applications. Zinc oxide has an immense potential for use in the electronics industry. As far as the piezoelectric applications are concerned, it is thermally stable and has a coupling coefficient close to that of lithium niobate.

Zinc oxide is a wide-band-gap material and has a tendency to grow with non-stoichiometry, with extra zinc, whether interstitial zinc or vacancies of oxygen are responsible for the non-stoichiometry, has not been established yet [12, 13]. Its conductivity can be varied by the control of growth conditions and judicious use of dopants. Zinc oxide is transparent

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to light. Thin films of ZnO are being widely studied for use as optical waveguides and acousto-optic media. Zinc oxide films on semiconductor substrates are potentially useful in heterojunction solar cells [14] and SAW signal processing [15].

B. Growth Systems

A wide range of methods exist for the growth of epitaxial films. The methods can be broadly classified into two categories--physical and chemical. Out of the physical methods, sputterings have been used for growth of piezoelastic films. Out of the chemical methods, chemical vapor deposition and transport methods have been successfully employed for growing piezoelectric films of AlN and ZnO on sapphire. CVD epitaxy has the following advantages:

   i)   Growth conditions are closer to equilibrium at the
        growing surface.

   ii) A choice of reactions and starting materials is available.

   iii) Doping during growth is possible.

   iv) Because of the higher growth temperature and advantage
        (i) above, epitaxial films have better quality than
        sputtered films.

B.1 Aluminum Nitride Growth

Aluminum nitride has been grown by various techniques such as glow-discharge, reactive evaporation, chemical and plasma-chemical vapor deposition and closed-space vapor transport processes. Some of the published results on various growth systems are tabulated in Table 1.

TABLE 1

AlN CVD Growth

Reference Author Year	Reaction/Method	Substrate	Temp., $^{\circ}$C	Remarks
Chu [1] 1967	$AlCl_3 + NH_3$	SiC, AlN	1200-1250	s.c.
Cox [2] 1967	Elec. discharge Al electrodes N_2 atm.	sapphire	1780	p.c.
Portnoi [3] 1973	$Al_2O_3 + 3C + N_2 = 2AlN + 3CO$		1800-2050	Fe impurity, Whiskers
Duffy [4] 1973	$TMA + NH_3$	sapphire spinel	1200-1250	Epitaxial
Uemura [5] 1974	Glow discharge Al films in N_2 atm.	Al		p.c.
Callaghan [6] 1974	$AlCl_3 + NH_3$ vap. phase dep.	sapphire	800-1250	(0001) s.c. (01$\bar{1}$2) p.c.
Chu & Kelm [7] 1975	$AlCl_3 \cdot 3 NH_3$	Si	800-1200	p.c.
Yoshida [8] 1975	Reactive evap. of Al in NH_3		1250	
Lakin & Liu [9] 1976	TMA & NH_3	sapphire	1200	s.c. with some 2-D growth
Bauer [10] 1977	Chemical & plasma-chemical vap. dep. $AlCl_3 + NH_3$		700-1300	
Perry & Rutz [11] 1978	Closed space vap. transport		1800	s.c.

Films have been grown on insulating and semiconducting substrates such as sapphire, spinel and silicon, etc. Films of varying quality ranging from single crystalline to polycrystalline have been achieved at growth rates ranging from 2000 A$^\circ$/hr. to 30 μm/hr. The epitaxial temperature is found to be around 1200-1250°C. However, thick single crystal films of good quality have not been reported to date.

In the present study CVD was developed as a growth technique for films of AlN on sapphire, suitable for temperature-stable, high frequency SAW devices. Reaction of trimethyl aluminum (TMA) with ammonia in hydrogen atmosphere was pursued in view of the distinct advantages afforded by the use of metal-organics, e.g., the ease of control of the amount of reactants, the ease of doping by use of metal-organic source for the dopant and the possibility of reduction of the growth temperature.

B.2 Zinc Oxide Growth

Zinc oxide thin films for piezoelectric applications have been successfully grown by sputtering. Some of the reported sputtering parameters are listed in Table 2. It is difficult to grow good quality films at a reasonable rate using the various sputtering methods, with the exception of planar magnetron sputtering [31]. 10 μm thick films exhibiting mirror finish have been grown by this technique. Several vapor epitaxial growth techniques have been used to grow thicker films of ZnO on sapphire, however, most of these yield films showing large surface roughness. Most of the reported methods (see Table 3) are based essentially on vapor transport using H_2/H_2O or $H_2/H_2O/HCl$ as transport agents.

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TABLE 2

ZnO Sputtering

Reference	Method	Substrate	Temp., $^{\circ}$C	Dep. rate A°/min	Remarks
Rozgonyi [16] 1966	d.c.	sapphire	175	< 130	
Bahr [17] 1972	d.c. & r.f. with mag. field		18-140°	50	
Khuri-Yakub [18] 1975	r.f. with mag. field	sapphire	> 350	130	
		Si/SiO$_2$	250		
		Au	225		
Paradis & Shuskus [19] 1976	r.f. with mag. field	sapphire	465-575	< 100 \ 2	$\rho > 10^6 \Omega$-cm \ 80:20 Ar:O$_2$
Ohji [20] 1978	hemis-pherical r.f.	glass	100-220	50-130	50:50 Ar:O$_2$
Wasa & Hayakawa [21] 1978	d.c. magnetron		40-270	160	
Shiosaki [31] 1978	planar magnetron	glass, metal	340	500	50:50 Ar:O$_2$

TABLE 3

ZnO Growth by CVD

Reference	Reaction/ Method	Growth Temp., °C	Growth Rate μ/hr.	ρ (Ω cm)/ Remarks
Ryabova [22] 1968	$(C_2H_7O_2)_2$ Zn pyrolysis	600-680	.0600	$10^5 - 10^8$
Rabadanov [23] 1970	$ZnO + H_2 =$ $Zn + H_2O$ Transport	550-650	—	1
Galli & Coker [24] 1970	$ZnO + H_2 =$ $Zn + H_2O$ $ZnO + 2HCl =$ $ZnCl_2 + H_2O$	775	50	1-10/transport
Reisman [25] 1973	$Zn + H_2O$ Controlled P_{Zn}/P_{H_2O}	800-900	3-20	1/oxidation of Zn vapor
Quon & Malanka [26] 1975	$ZnO + H_2 + HCl$ Transport	590-632	120	—
Ohnishi [27] 1978	$ZnO + H_2 + H_2O + O_2$	975	720	Intermediately sputtered sapphire substrate
Clarke [28] 1978	Transport using CO	800	—	polycrystalline deposits on quartz tube

Others use evaporation of metallic zinc and its subsequent oxidation to zinc oxide using wet hydrogen [25]. Thin films grown by these methods always exhibit resistivity of $1\text{-}10\ \Omega\text{-}cm$ and are thus unsuitable for direct use and in the past, diffusion of lithium into the films has been used to improve the resistivity.

ZnO growth using a metal-organic zinc source, DEZ (Diethyl Zinc), and N_2O/N_2, H_2O/H_2 and $CO_2/H_2/N_2$ as oxidizing agents was investigated in the present study. Zinc oxide films were grown on sapphire by MO-CVD, and by planar magnetron sputtering on sapphire and Si/SiO_2 substrates. The substrates were given various pre-growth treatments as described elsewhere. The films were studied under optical and scanning electron microscopes and analyzed using X-ray diffraction, RED, etc. As a routine thickness measurements were made by a stylus instrument (Dektak) and piezoelectric measurements were made on good quality films using a network analyzer.

II. EXPERIMENTAL RESULTS AND DISCUSSION

A. AlN Growth

A systematic study of such parameters as gas composition and flow rates, injection tube geometries and substrate temperature has been conducted with the quartz bell jar experimental configuration (Fig. 1). Typical growth parameters are listed below:

Substrate Treatment: H_2 etch for 15 minutes at $1250^{\circ}C$
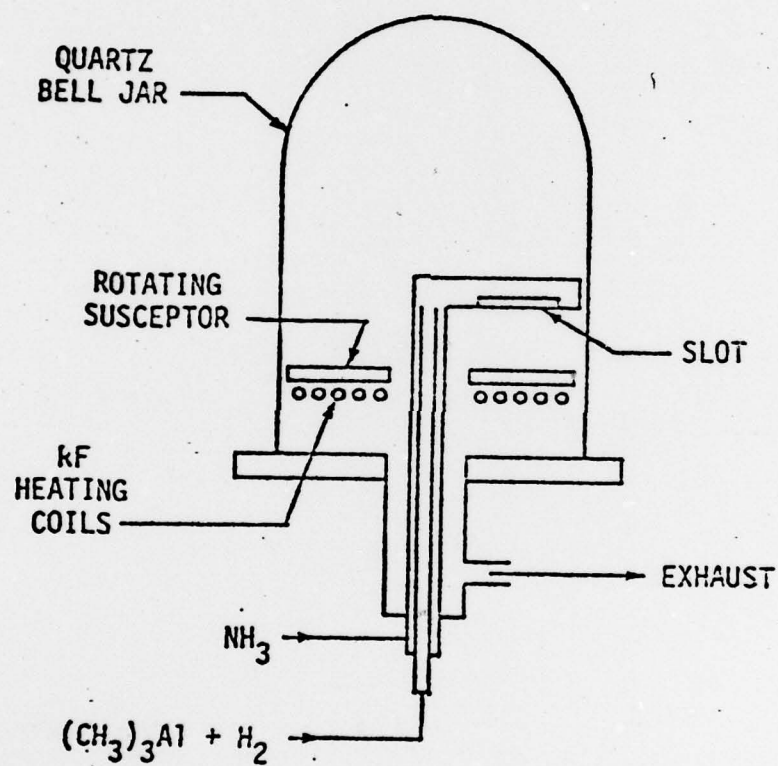
Gas flow rates during growth:

H_2:   8.5 ℓ/min.

QUARTZ
BELL JAR

ROTATING
SUSCEPTOR

SLOT

kF
HEATING
COILS

EXHAUST

NH$_3$

(CH$_3$)$_3$Al + H$_2$

FIGURE 1   Experimental configuration for CVD

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NH_3:   1.1 ℓ/min.

TMA: 0.017 ℓ/min.

Growth temperature: 1200°C

Typical growth time: 40-90 minutes.

The reaction between TMA and NH_3 begins at room temperature, with formation of a solid compound $(CH_3)_3Al:NH_3$ which then proceeds to dealkalyze with increasing temperature to finally release AlN solid at some temperature higher than 160°C. The injection tube in the configuration of Fig. 1 passes through the hot susceptor, thus the reactant gases must be separated. Therefore, a concentric injectin tube must be used to direct the gases onto the substrate.

Films up to 10 μm thickness, exhibiting excellent chemical and mechanical stability together with consistent surface acoustic wave parameters have been achieved. X-ray diffraction and SEM were used for the determination of the quality of the films. It was observed that high flow rates of reactants are required for growth of AlN films at reasonable growth rates. Growth is thus mass transport limited at the optimum temperature of ~ 1200°C. Thus a boundary layer of gases above the substrate defines the concentration gradient of the reactants from the mainstream value to that in equilibrium with the growing surface. Intermediate compound formation and their subsequent dissociation at the surface may be responsible for disruption of streamline flow. Use of very high injection velocities, however, causes other problems, namely, 3-D nucleation in the gas stream and 2-D nucleation at the surface as confirmed by SEM examination.

In the course of the study it was found that the film quality is critically dependent upon substrate cleaning procedure. Even though a

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standard polishing and cleaning procedure was always followed, film quality could not be controlled. Identical experimental conditions did not yield films of same quality. In view of this, the need for a standard substrate handling procedure was felt. Hydrogen etching at a temperature of 1250°C for 15 minutes was therefore selected to give sapphire of reproducible surface.

The other important factor was found to be the purity of the H_2 gas. Since Al_2O_3 is a more stable compound than AlN, the minutest quantiti es of oxygen , moisture, CO_2 or CO can cause the formation of Al_2O_3, which can interfere with epitaxial growth. Thus minutest quantities of oxidizing gases in the system are detrimental to film quality.

Film growth was generally found to be slow and non-uniform. SEM examination of the films showed the presence of 2-D facets and sometimes even 3-D growth (see Fig. 2). For some samples C-axis of the growing grains was found to be pointing upwards.

The bad quality is attributed to the following:

i)   Too high arrival rates of gaseous reactants with the resultant 2-D nucleation on the surface.

ii) 3-D nucleation on the injection tube wall (which gets hot in the present geometry) and in the gas stream, the nucleii formed falling on the growing surface; and

iii) The absence of uniform nucleation sites on the sapphire substrate.

In the deposition of epitaxial thin films, an important point to consider is the fact that nucleation and growth of films are two distinct processes, and that the optimum conditions for one may not be the optimum
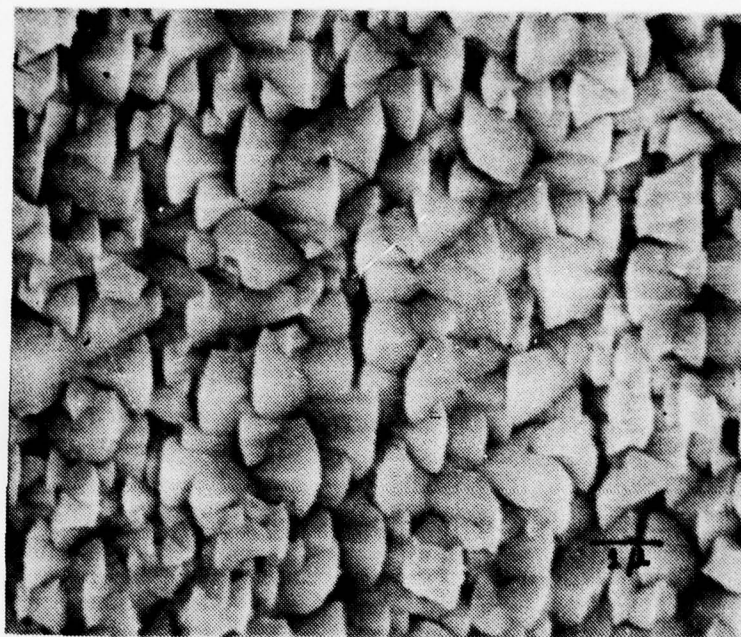
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Figure 2.   Scanning electron micrograph of AlN on

R-plane sapphire showing 2-D growth.

conditions for the other. In order to grow a good epitaxial film one must optimize the conditions for the two stages separately.

In the case of growth of AlN on sapphire by CVD, it is seen that the average crystallite size is a few microns. It is possible to grow a film of a few micron thickness at a reasonable rate. But if one tries to reduce the growth rate with an idea of improving the quality of the film, no or little growth takes place. On the other hand, efforts to grow very thick films at a fast rate end up in band quality films. These observations indicate that the growth of the crystallites start at nucleii that develop at defect sites on sapphire, which are on the average more than a few microns apart. Nucleii do not form on the defect-free sapphire substrate because of the high interface energy between sapphire and AlN. In such a situation efforts to improve the quality of the substrate will result in a smaller number of nucleii per unit area, which will yield a rugged-surfaced film with two-dimensional crystallites because of the little interaction between the growing nucleii.

In order to grow a good film one needs a large number of nucleii per unit area during the initial stages of nucleation. Once a very thin layer has formed, the growth method or parameters should be changed to optimize the film growth process.

In view of the above, the following methods are suggested for improving the nucleation of the film.

a) Etching the substrate to give a dense, uniform defect density. Chemical etching or thermal etching in a suitable gas atmosphere may be tried.

b) Growing a very thin film of AlN on Al_2O_3 by reaction with NH_3 at Temp. $\geq 1500^{\circ}C$.

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c) Nucleating a thin film by sputtering.

It is well known that sputtering gives uniform films with a high density of nucleii, due to the high momentum of the sputtered particles, which get embedded in the substrate and thus have a higher sticking efficiency. The orientation of the layers grown by sputtering should depend upon the orientation of the substrate; i.e., (0001) should grow on (0001) sapphire and ($1\bar{2}10$) on R plane sapphire.

Since AlN is unstable in air and a thin surface layer (50 $\mathring{A}$) reacts with oxygen resulting in the formation of aluminum oxide, the sputtered substrate has to be quickly transferred into the CVD unit. A high substrate temperature (1500°C) is needed for conversion of Al_2O_3 into AlN by the following reaction:

$$Al_2O_3 + 2\ NH_3 \rightleftharpoons 2\ AlN + 3\ H_2O$$
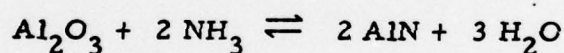
The growth system must be capable of sustaining high temperatures and low oxygen partial pressure.

B. ZnO Sputtering and CVD Growth

B.1 Sputtered Films

Good quality films with smooth surfaces have been grown under the following deposition conditions in an r.f. diode sputtering unit.

>Target: ZnO
>Pressure: ~ 10 μ
>Input Power: 300-400 W
>Target Voltage: 550-1000 V

Source to Substrate Distance: 3.75 cms

Sputtering atmosphere: 20% O_2 in Ar and

50% O_2: 50% Ar

Substrate	Temperature, $^\circ$C	Dep. Rate, μ/hr.
Sapphire	350	0.75
Si/SiO$_2$	175-200	0.7
Si/Au	150	0.4

SEM examination of a 4-5 μm thick film grown on sapphire shows dense, fine-grained microstructure with a grain size ~ 1 μm. Sections of films grown on (100) Si/SiO$_2$ when examined under SEM show preferred orientation with C-axis perpendicular to the plane of the substrate.

The films are transparent but have a yellowish color when grown in 20% O_2 in Ar atmosphere. The resistivity of as-grown films was ~ 10^5 Ω-cm but could be increased by several orders of magnitude by annealing in air at 800°C for an hour. The yellow color disappeared during this treatment.

Planar magnetron sputtering increased the growth rate to a few microns per hour with an input power of only 150 W. Films thicker than a few microns could not be grown in the present geometry (target above substrate) because of the problem of falling of loose fine powder on the substrate. The unit is now being modified in order to invert the geometry.

B.2 CVD Growth of ZnO

Chemical vapor deposition of ZnO on sapphire was investigated

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using diethyl zinc as the zinc source and N_2O/N_2, H_2O/H_2 and $CO_2/H_2/N_2$ as the oxidizing gas mixtures. Table 4 shows the growth parameters and Figs. 3 and 4 show the variation of the growth rate with temperature and N_2O, H_2O or CO_2 flow rate for the three reaction systems. Figure 5 shows the scanning electron micrograph of the film surface grown by the DEZ/N_2O process. The micrograph shows hexagonal needles of ZnO growing out of the sapphire substrate with C-axis almost perpendicular to the substrate surface. Also, the needles are well separated leaving voids in between.

N_2O is a buffered oxygen source and needs a temperature of at least $700^\circ C$ for dissociation. The optimum temperature for growth is about $730^\circ C$ and at this temperature N_2O transforms the surface of sapphire in such a way that the epitaxial relationship is lost.

Figure 6 shows the schematic diagram ofthe CVD system used for the $DEZ/H_2O/H_2$ process. The substrates were etched at $\sim 1200^\circ C$ in H_2 for about 30 minutes. Table 4 lists the growth parameters. X-ray diffraction patterns were inconclusive regarding the orientation of the films and SEM examination revealed no apparent texture (Fig. 7). Evidence of 3-D overgorwth, even in the early stages of growth, was found. This could be related to nucleation within the injection tube. RED of 3 μm thick film indicated polycrystalline microstructure with some preferred orientation (Fig. 8).

The possible reactions in the $DEZ/H_2/H_2O$ growth system are given below.
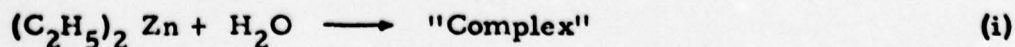
At room temperature:

$$(C_2H_5)_2 \, Zn + H_2O \longrightarrow \text{"Complex"} \tag{i}$$

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TABLE 4. Growth of ZnO on Sapphire by MO-CVD

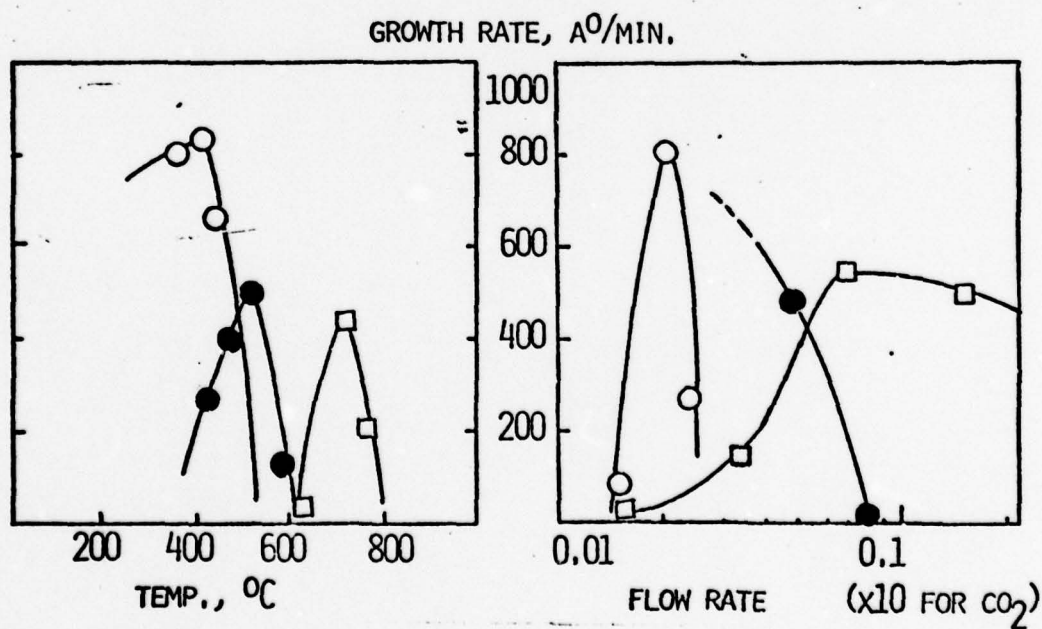| Process	Growth Temp., $^{\circ}C$	Growth rate, $A^{\circ}/min.$	Film Quality of Nature	Elec. Resistivity (ohm-cm)
DEZ + N_2O/N_2	730	300-500	hexagonal needles	10^2
DEZ + H_2O/H_2	400	300-850	oriented p. c.	10^0 - $10'$
DEZ + CO_2/H_2	520	500	oriented p. c.	10^6

GROWTH RATE, $A^{\circ}/MIN.$

Fig. 3. Growth rate as a func-
tion of temperature
for H_2O (o), N_2O (□)
and CO_2 (•) systems

Fig. 4. Growth rate as a func-
tion of flow rate of
H_2O (o), N_2O (□) and
CO_2 (•).

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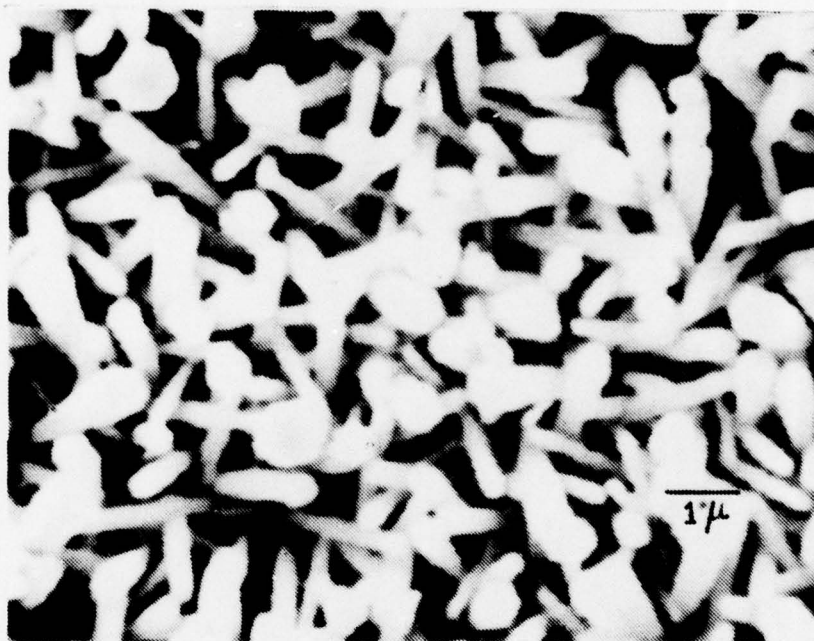
Fig. 5   Scanning electron micrograph of ZnO on R-plane
          sapphire, grown by the N_2O/DEZ process,
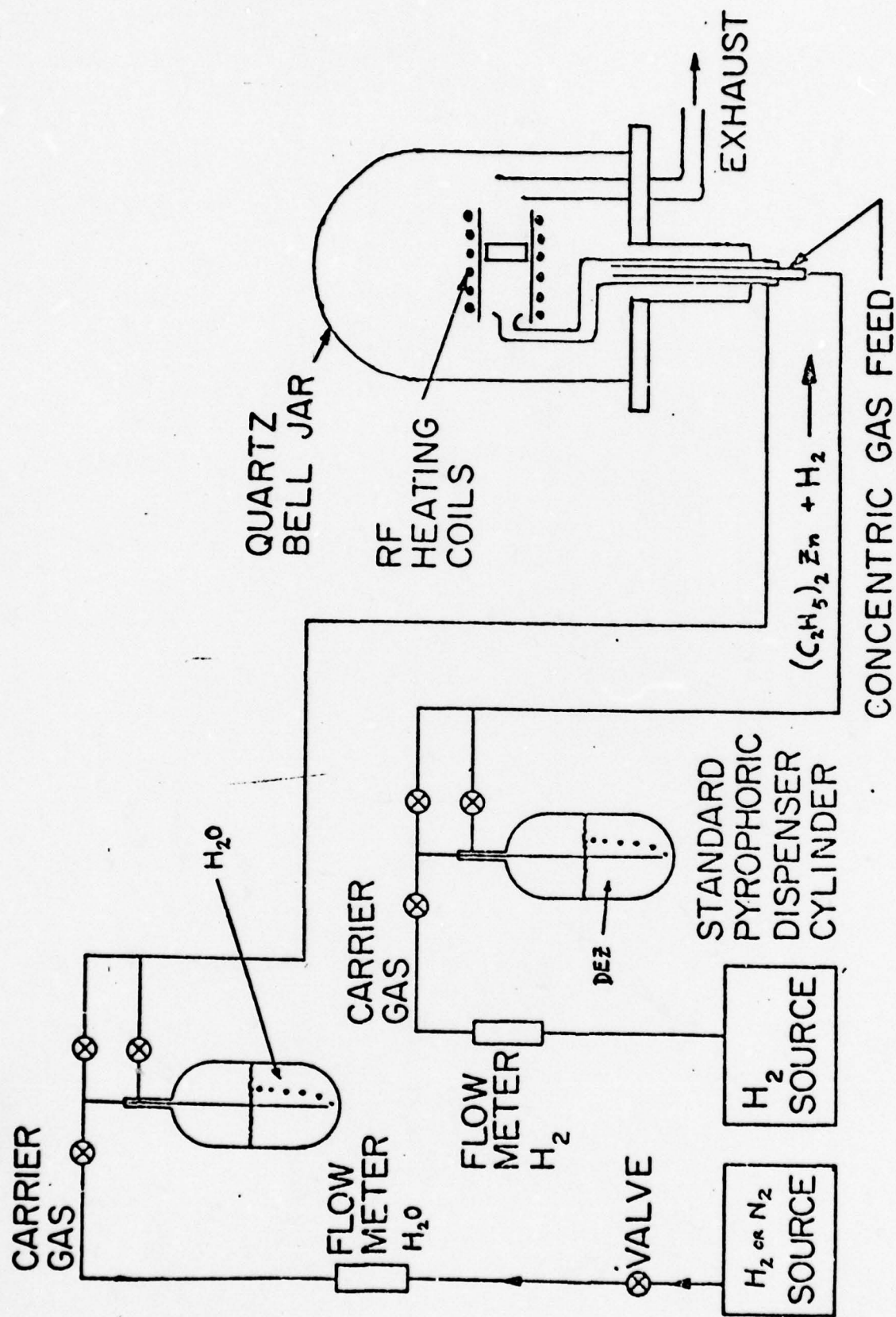   showing hexagonal needles.

Fig. 6   Schematic diagram of the CVD system used for ZnO Growth

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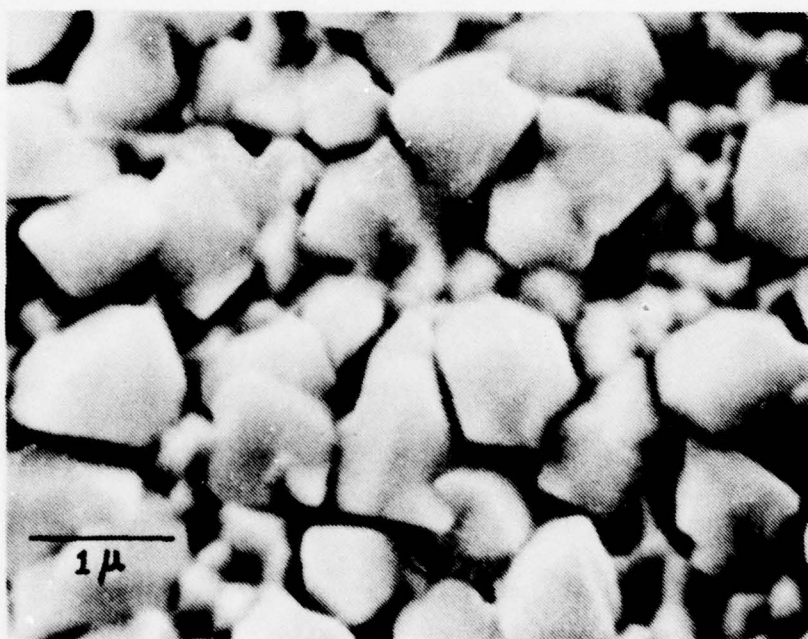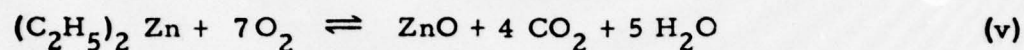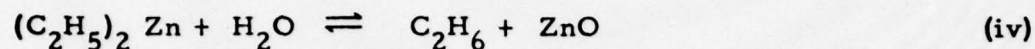
Fig. 7   Scanning electron micrograph of ZnO/sapphire

grown by the $H_2/H_2O/DEZ$ process.

Fig. 8   RED pattern of a ZnO film grown on R-plane

sapphire by the $H_2/H_2O/DEZ$ growth process.

At high temperature near/on the substrate:

$$H_2O \rightleftharpoons H_2 + \tfrac{1}{2} O_2 \qquad\qquad\qquad\qquad\qquad (ii)$$

$$\text{"Complex"} \rightleftharpoons ZnO + C_2H_6 \qquad\qquad\qquad\qquad\qquad (iii)$$

$$(C_2H_5)_2 Zn + H_2O \rightleftharpoons C_2H_6 + ZnO \qquad\qquad\qquad\qquad (iv)$$

$$(C_2H_5)_2 Zn + 7 O_2 \rightleftharpoons ZnO + 4 CO_2 + 5 H_2O \qquad\qquad\qquad (v)$$

Exothermic reaction (v) seems to be unlikely under the highly reducing conditions used.

The rate of growth of the film should be given by

$$r \propto P_{H_2O} \cdot P_{DEZ} / P_{H_2}$$

The rate of growth of the ZnO film is found to increase with increasing total gas flow, indicating mass transport limited growth. Temperature also has a large effect on the growth rate as is evident from Fig. 3. The nature of the curve indicates that the overall dominant reaction has a negative free energy change. Thus at low temperature, the reaction is kinetically controlled (probably a high activation energy is needed for the dissociation of the complex formed) and at high temperatures growth rate drops due to thermodynamic factors. Figure 9 is a diagramatic representation of the variation of the growth morphology of ZnO with variation of temperature and H_2O/H_2 ratio. Good quality films could be achieved at a temperature around $400^\circ C$ at a growth rate of $800 \, \overset{\circ}{A}/minute$.
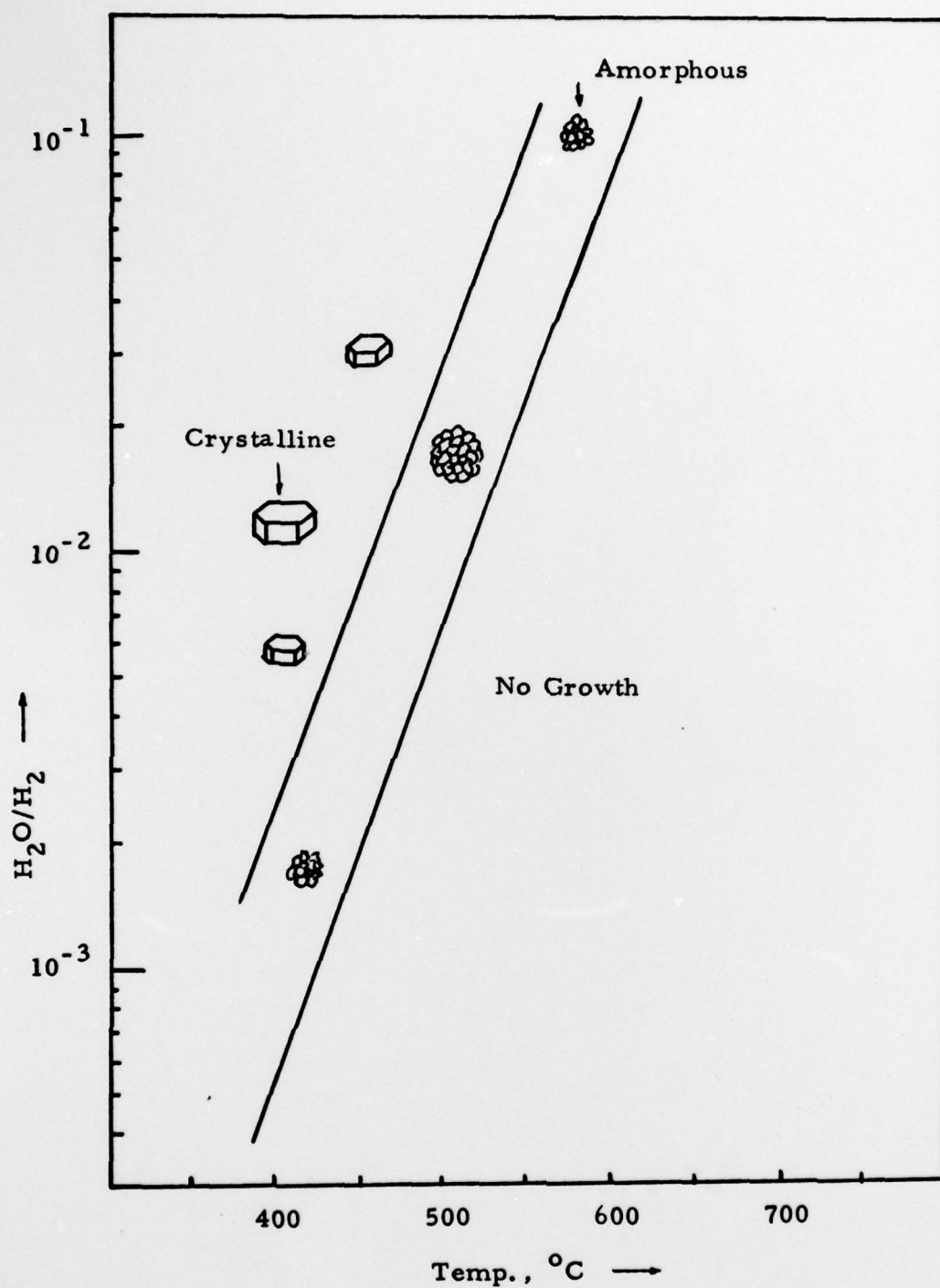
Fig. 9 Diagramatic representation of the growth morphology as a function of temperature and H_2O/H_2 ratio for ZnO growth by the $H_2/H_2O/DEZ$ system.

Electrical resistivity of the films was found to be around 1-10 ohm-cm, much lower than sputtered films and could be increased to around 10^6 ohm-cms by annealing in air. Annealing in oxygen or air should reduce non-stoichiometry and thereby reduce the number of vacancies of oxygen (or zinc interstitials) which act as donors. Annealing in air at 800-850°C for 1 hour should reduce propagation losses.

Diffusion of lithium into the films using a Li_2CO_3 source increased the resistivity by several orders of magnitude. Since as grown ZnO is always found to be n-type presumably due to the presence of $V_O^{\cdot}$ or zinc interstitials which act as donors, lithium, which is an amphoteric dopant in ZnO needs a special heat treatment in a certain p_{O_2} for effective compensation.

The problem of the low resistivity of as-grown films has been solved by the use of CO_2 as the oxidizing gas, using the DEZ/CO_2 reaction for the formation of zinc oxide. Again, dense films with very fine microstructure (grain size $< 1 \mu m$) are achieved. CO_2 has been known to get adsorbed on ZnO surfaces and increase the surface resistivity. Thus, during this growth process, carbon may get incorporated into the film and the formation of other donors like zinc or hydrogen interstitials may become unfavorable. These films have such high resistivity that after-growth diffusion is not needed.

C. Electrical Characterization

C.1 Piezoelectric Measurements

The surface acoustic wave parameters, K^2--electromechanical coupling coefficient, V_s--propagation phase velocity, and propagation

loss have been measured for AlN films for t/λ (film thickness/transducer wavelength) values of 0 to 0.75. The effect of the sapphire substrate upon the SAW parameters is still present at t/λ of 0.75 [29].

Bulk material SAW values for AlN are not available because of difficulty of growing bulk AlN. To infer bulk material characteristics, thicker AlN films will be grown and at the same time, we will make masks of transducers with shorter wavelengths (or higher frequencies) with presently available photolithographic and reduction equipment. This will in effect enable measurements to be made for AlN at larger t/λ's, to the point ($t/\lambda > 2$), where the effect of the substrate is reduced to vanishing and the main portion of the surface wave is in the AlN film.

At high frequencies, SAW parameter measurements are extremely sensitive to surface finish and material quality [30]. It is important that measurements for thicker films where surface morphology becomes very rough due to increased crystallite size take these effects into account to present a true picture of material characteristics.

At present, transducers of 10 μ wavelength (600 MHz for AlN0 can be produced upon samples. Increasing AlN film thickness (to 15 μ) while producing transducers of shorter wavelengths (e. g., 6 μ or 1 GHz for AlN) would enable measurements to be made out to the t/λ's of 2.5, where the effect of the substrate upon the SAW would be negligible.

C. 2 Temperature Coefficient of Delay Measurements

Temperature coefficients of delay of AlN have been measured for t/λ's up to 0.6. With increasing t/λ from zero, the value decreases from a positive value corresponding to that for sapphire, ~ 47 ppm/°C, to

approximately 24 ppm/$^\circ$C for the AlN/Al$_2$O$_3$ composite with t/λ = 0.6.
Evidence points strongly to the possibility that AlN has a negative
temperature coefficient of delay. Hence, a temperature stable composite
AlN/Al$_2$O$_3$ can be made with t/λ corresponding to the AlN film thickness
where temperature coefficient equals zero.

III. CONCLUDING REMARKS

Distinct advantages are afforded by the use of metal-organics in
chemical vapor deposition. However, coupled with their use, are the
disadvantages related to the facts that very little thermodyanic data are
available, a number of reactions can take place and complexes are formed
at low temperatures. Therefore, one cannot theoretically predict the
optimum conditions for growth.

The nature and extent of nucleation of thin films on sapphire are
a function of the state of its surface, its degree of perfection and cleanliness,
etc. This brings in another important parameter in the growth of thin
films by the metal-organic process on sapphire. The present study has
shown that there is need for a substrate treatment process prior to thin
film growth.

More work is necessary to realize the full potential of AlN thin
films on sapphire. Investigations into top feeding of reactants in AlN CVD
growth and doping of AlN during growth will be investigated next. In the
case of ZnO, a planar magnetron sputtering unit has been set up and will
be used to grow thick ZnO films on sapphire and silicon. A horizontal
quartz tube system has been assembled to study in detail the growth of
ZnO on sapphire. Efforts will be made to incorporate lithium into the

films during the growth. Various substrate pre-treatment procedures are being tried, including pre-sputtering of a very thin ZnO layer on the sapphire substrate prior to growth by chemical vapor deposition.

In CVD growth, the lowest possible temperature resulting in epitaxial films, must be employed for growth. Films grown at higher temperatures react with the sapphire substrate, and the interface gives rise to increased wave guide propagation losses.

The H_2O/DEZ process shows promise as a low temperature growth process for growing ZnO thin films. The CO_2/DEZ process uses slightly higher temperature but eliminates the necessity of post-growth diffusion, as the resistivity of the as-grown films is very high.

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APPENDIX A

Growth of ZnO Thin Films by MO-CVD

Extended Abstract of the paper to be presented at the October meeting of the Electrochemical Society at Los Angeles, California.

GROWTH OF ZnO THIN FILMS BY MO-CVD

Chi Kwan Lau, Shiban K. Tiku and Kenneth M. Lakin
University of Southern California
Los Angeles, California 90007

Zinc oxide is a thermally stable piezoelectric material with a coupling coefficient close to that of lithium niobate, and has a potential to replace the currently used materials in acousto-electric, acousto-optic, photoconductive and electro-optic applications. The $(11\bar{2}0)$ ZnO on $(01\bar{1}2)$ sapphire heteroepitaxial system is of particular interest. Zinc oxide layers are easy to prepare and exhibit a crystalline perfection much superior to AlN. Zinc oxide films have been grown by sputtering, however, good quality films cannot be grown at a reasonable rate. Vapor transport methods yield films having large surface roughness and high conductivity making post-growth annealing, polishing and compensation necessary.

The use of metal-organics seems attractive for the growth of these films as a lower epitaxial temperature may be achieved. We investigated the growth on sapphire from diethyl zinc (DEZ) using N_2O/N_2, H_2O/H_2 and CO_2/H_2 as the oxidizing gas mixtures. The substrates were placed inside an r-f heated horizontal quartz tube assembly. Pressures lower than atmosphere and high gas flow velocities near the substrate were used. A standard substrate handling procedure, consisting of hydrogen-etching the chemically polished sapphire at 1250°C for 1/2 hour just before growth, was followed. The films were examined using optical and scanning electron microscopes and analyzed using x-ray diffraction, RED, etc.

Table 1 shows the growth parameters for the three systems studied.

Films grown by the $DEZ/N_2O/N_2$ process, showed hexagonal needles of ZnO growing out of the sapphire substrate with C-axis almost perpendicular to the substrate surface. Also, the needles were well separated leaving voids in between. N_2O is a buffered oxygen source and needs a temperature of at least $700^{\circ}C$ for dissociation. The optimum temperature for high growth rate is about $730^{\circ}C$, at this temperature N_2O transforms the surface of sapphire in such a way that the epitaxial relationship is lost.

DEZ and H_2O react at room temperature to form a complex which dissociates to give a dense ZnO film at the hot substrate surface. SEM examination did not reveal needles or faceting. However, evidence of some 3-D growth even in the early stages of growth was found. RED examination of a 3 μm thick film grown at $\sim 400^{\circ}C$ revealed polycrystalline microstructure with highly oriented regions. The $DEZ/CO_2/H_2$ system gave dense films, with high electrical resistance. Characterization of these films is in progress.

The design of the growth system, distance of the injection tube from the substrate, the temperature at which the reactants are mixed and the velocity of the gas stream are all important in determining the growth rate.

Figures 1 and 2 show the variation of the growth rate with temperature and N_2O, H_2O and CO_2 flow rates for the three systems. The temperature ranges available for growth are narrow and excess of both DEZ and the oxidizing gas are found to reduce the growth rate indicating poisoning of the growing surface. Hydrogen and other species present (e.g., CO) are probably adsorbed at the growing surface and play an important part in the growth mechanism, and may be present in the as

grown films. From a consideration of the optimum growth temperature and the high resistivity, DEZ/CO_2 system appears to be the most promising for growing epitaxial films of ZnO.

TABLE 1.   Growth of ZnO on Sapphire by MO-CVD

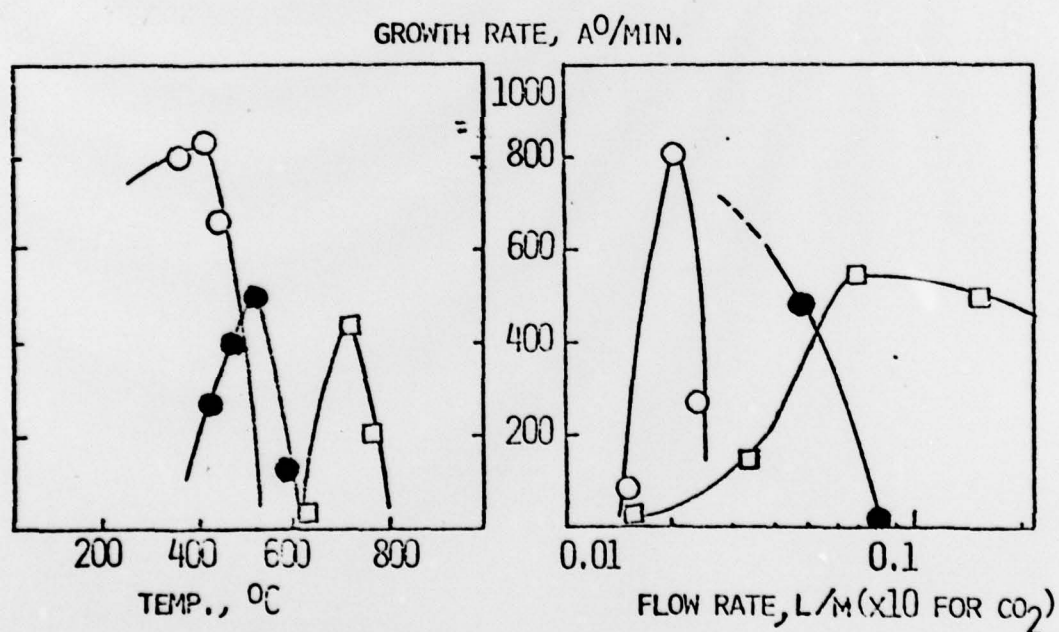| Process	Growth Temp., °C	Growth rate, A°/min.	Film Quality or Nature	Elec. Resistivity (ohm-cm)
DEZ + N_2O/N_2	730	300-500	hexgonal needles	10^2
DEZ + H_2O/H_2	400	300-850	oriented p. c.	10^0-$10'$
DEZ + CO_2/H_2	520	500	oriented p. c.	10^6

Fig. 1. Growth rate as a function of temperature for H_2O (o), N_2O (□) and CO_2 (•) systems.

Fig. 2. Growth rate as a function of flow rate of H_2O (o), N_2O (□) and CO_2 (•).

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This report includes the details of research work on this two-year project on the growth and chcaracterization of thin films for piezoelectric applications. The report covers the results on AlN and ZnO growth by the metal-organic process. The problems associated with the AlN on sapphire system have been discussed. In the case of ZnO films, low temperature CVD system (DEZ/H_2O and DEZ/CO_2) have been developed. It is seen that the films grown by the DEZ/CO_2 system do not need any post-growth diffusion, as the as-grown resistivity is quite high.

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